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Edito

We are happy to send you the fourth edition of the "CEMES Highlights" for the year 2019.

2019 was the 80th anniversary of the CNRS and among many events to celebrate it, one important for CEMES was the inauguration on September the 24th of the first international joint laboratory between the CNRS and a foreign company: Hitachi High Technologies. The HC-IUMi joint laboratory, namely "Hitachi-CNRS Infrastructure for Ultrafast Microscopy," aims at developing a coherent time-resolved electron microscope by combining the recent developments of high brightness pulsed electron sources triggered by a femtosecond laser carried out in CEMES and the HHT expertise in advanced electron microscopes.

The 2019 issue of the CEMES Highlights magazine makes a focus on 10 articles published this year on original scientific advances carried out in our laboratory. The list is far from being exhaustive, and a much more complete overview of our publications can be found in the Open Access HAL collection of CEMES.

Several CEMES members were distinguished for their work this year, including Florent Houdellier who received the Ernst Ruska 2019 prize from the German Microscopy Society and Andrej Jancarik, the "Young investigator award 2019 ICT" prize for his work on the new ways of synthesis of alkenes.

2019 was also the starting year of the 4 years "ESTEEM3" (Integrated Infrastructure H2020) project in the continuation of the ESTEEM (FP6) and ESTEEM2 (FP7) projects with an enlarged European consortium. ESTTEEM3 aims at providing access for the academic and industrial research community in materials science to the most powerful TEM techniques available at the nanoscale.

These yearly booklets aim at presenting the different experimental facilities hosted at CEMES and this year we make a focus on the Clean Room nanofabrication capacities the laboratory has recently developed and is offering to the local scientific and industrial communities.

An overview of our activities can be found on our website www.cemes.fr, which details in particular the research work of each of the 7 research groups of the CEMES laboratory.

We wish you an interesting reading of this 2019 issue of the CEMES Highlights



Etienne Snoeck, Alain Couret CEMES director and deputy director

Édito

Nous sommes heureux de vous envoyer la quatrième édition des "Highlights du CEMES" pour l'année 2019.

2019 a été l'année du 80e anniversaire du CNRS et parmi les nombreux événements qui l'ont célébré, l'un des plus importants pour le CEMES a été l'inauguration le 24 septembre du premier laboratoire commun international entre le CNRS et une société étrangère : Hitachi High Technologies. Le laboratoire commun HC-IUMi, (Hitachi-CNRS Infrastructure for Ultrafast Microscopy) vise à développer un microscope électronique à résolution temporelle cohérent en combinant les développements récents au CEMES de sources d'électrons pulsés à haute luminosité déclenchées par un laser femtoseconde et l'expertise HHT dans les microscopes électroniques avancés.

Ce recueil des Faits-Marquants 2019 du CEMES met l'accent sur 10 articles publiés cette année sur des avancées scientifiques originales réalisées dans notre laboratoire. La liste est loin d'être exhaustive, et celle complète de nos publications se trouve dans la collection HAL Open Access du CEMES.

Plusieurs membres du CEMES ont été distingués pour leur travail cette année, notamment Florent Houdellier qui a reçu le prix Ernst Ruska 2019 de la German Microscopy Society et Andrej Jancarik, le prix Jeune Chercheur 2019 de l'ICT pour son travail sur les nouvelles voies de synthèse des alcènes.

2019 a également été l'année de démarrage du projet «ESTEEM3» (Integrated Infrastructure H2020) qui s'inscrit dans la continuité des projets ESTEEM (FP6) et ESTEEM2 (FP7) avec un consortium européen élargi. ESTEEM3 vise à donner accès à la communauté académique et industrielle de la recherche en science des matériaux aux techniques TEM les plus puissantes disponibles à l'échelle nanométrique.

Dans ces brochures annuelles, nous souhaitons également présenter les différents moyens expérimentaux du CEMES. Cette année nous mettons l'accent sur les moyens de Nanofabrication en salle blanche que le laboratoire a récemment développés et offre aux communautés scientifiques et industrielles locales.

Un aperçu de l'ensemble de nos activités est disponible sur notre site www.cemes.fr qui détaille notamment les travaux de recherche de chacun des 7 groupes de recherche du laboratoire CEMES.

Nous vous souhaitons une lecture intéressante des Faits-Marquants 2019 du CEMES.



Etienne Snoeck, Alain Couret Directeur et directeur adjoint du CEMES



Pushing the limits of optical information storage using deep learning P. R. Wiecha, A. Lecestre, N. Mallet et G. Larrieu > Nature Nanotechnology 14, 237–244 (2019) https://doi.org/10.1038/s41565-018-0346-1

The internet, digital media and big data induced an explosion of the need for data storage capacity and unfortunately, with the data capacity, also an exponential growth of its energy consumption. Optical information storage is a promising approach to reduce energy requirements, but no successor to the "Blu-ray Disc" - state-of-the-art for almost 20 years - is in sight. We combine concepts of nanotechnology, photonics and artificial intelligence to increase storage density below the optical diffraction limit, the latter being the main physical challenge in going beyond the Blu-ray Disc.



Several bits of digital information are encoded in the geometry of silicon nanostructures, giving under polarized light unique optical scattering spectra for each encoded bit sequence. These spectra, strongly noisy, can nevertheless be decoded thanks to a network of artificial neurons, which was previously trained by learning on repetitions of nanostructures.

Our first key idea to overcome this limitation is to use silicon nanostructures and exploit their unique optical response over a broad spectral region for information encoding. While it is impossible to spatially resolve features below the diffraction limit from the optical far-field, deeply sub-wavelength geometric features can still have a strong impact on the optical scattering and therefore it is possible to observe their presence spectrally. We design silicon nanostructures encoding up to 9 bits of digital information. Attention is spent in the design of the geometries, such that every structure encoding a specific bit-sequence possesses a unique scattering signature. From the measured optical response, the encoded binary data can then be retrieved. Unfortunately, the

identification of the bit-sequences based on the scattering spectra becomes very difficult in realistic cases with structural defects and noisy measurements. The second key idea for the approach is therefore, to train a deep artificial neural network on the read-out of the encoded information via the optical spectra. We demonstrated, that using the combination of spectral scattering measurements and deep learning allows to encode and retrieve up to 9 bits of information from a diffraction limited area, effectively going beyond the information density of the Blu-ray.

Our results, published recently in Nature Nanotechnology [2], pave the way towards a next-generation optical storage concept with the potential to increase the information density by at least an order of magnitude.

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Strain relaxation of SGOI fabricated by the Ge condensation technique Warning ! Slippery interface

Strain evolution of SiGe-on-insulator obtained by the Ge-condensation technique

Victor Boureau, Shay Reboh, Daniel Benoit, Martin Hütch and Alain Claverie APL Mater. 7 (2019); doi:10.1063/1.5088441

Impact of Some Processing Steps onto the Strain Distributions in FD-SOI CMOS Planar Devices: A Contribution of Dark-Field Electron Holography

V. Boureau, D. Benoit and A. Claverie

ECS Journal of Solid State Science and Technology, 7 (9) P473-P479 (2018)

Studying in detail the impact of the fabrication steps of the n and p-MOS transistors on the crystalline deformations affecting the conduction channels of these transistors (Si for n-MOS, SiGe for p-MOS), CEMES researchers, in collaboration with Léti / CEA and STMicroelectronics, have demonstrated an unexpected stress relaxation mechanism in the SIGe-on-insulator structures, following the fabrication of SiGe by the so-called Ge condensation technique.

2	protective Pt deposit	(a)		(6
Sio	BOX			
STI	Si bulk		↑ <i>z</i> = [001]	
	ε _{xx} DFEH		$\stackrel{x=[110]}{\longrightarrow} R_{xz} DFEH \qquad \frac{50 \text{ nm}}{3}$	
1 de		(b)		(
	ε _{.x} .FEM -5%	5%	R _{xz} FEM -5°	5
-		(c)	and the second se	(9
-	s FEM thin elastic interface		R FEM thin elastic interface	

Strain and rotation maps from a SiGe-on-insulator layer, in the vi-cinity of a trench (STI); (a) and (e), measured by DFEH; (b) and (f), simulated by FEM "classical interface" and (c) and (g) simulated by introducing a thin and elastic interface.

In the "FD-SOI Transistors" technology deve-loped in particular by STMicroelectronics, the base wafer is formed of a thin layer of Si (10 nm) resting on top of an insulating silicon oxide layer. One of the difficulties to be overcome concerns the local transformation of Si into SiGe, required for the manufacture of high performance p-MOS in the vicinity of the Si-based n-MOS transistors. To do this, the technique called "Ge condensation" is used. It allows the gradual enrichment in Ge of a Si layer covered with an epitaxial SiGe layer during oxidation. During diffusion, the Ge atoms substitute from the Si atoms while keeping the "skeleton" of the silicon lattice in plane. The SiGe layer is then in compres-sion in this plane, which increases the hole mobility. mobility.

Measurements made on CMOS devices at the 24 nm node have demonstrated that the expected performances for the p-MOS on SiGe were not found, especially when the actives on which these transistors were ma-nufactured were small. In this context, CE-MES and STMicroelectronics undertook to

study the mechanical behavior of these layers during the manufacturing steps of p-MOS.

We therefore studied the evolution of the initial deformation in compression of the SiGe film during the fabrication of p-MOS transistors. For this, we compared the deformation maps of SiGe obtained by dark field electron holography with the results of numerical models des-Side obtained by dark field electron holography with the results of numerical models des-cribing the mechanics of the structure. In particular, we have shown unexpected behavior when the upper semiconductor is etched to fabricate the isolation trenches (STI) separating the Si n-MOS from the SiGe p-MOS. We note a dramatic and long-range relaxation of the SiGe layer initially in compression, without formation of extended defects. This phenomenon generates significant relative horizontal displacements between the SiGe layer and the underlying buried oxide (BOX). We suggest that the Ge-enrichment of the SiGe layer by the "Ge condensation" technique modifies the SiGe / BOX interface and that the observed stress relaxation results from the formation and propagation of interfacial defects from the edge to the center of the structure. In response to the biob shear stress present at the interface. to the center of the structure, in response to the high shear stress present at the interface.

These results not only make it possible to explain the electrical characteristics obtained on real devices but more importantly to propose alternative strategies (design) to keep the SiGe channels under compression and thus significantly improve the hole mobility in these devices



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Local chemistry as a tool to better understand the behauior of high performance aeronautical materials

Published in Material Science and Engineering A

Creep behavior in the new AD730TM nickel-based disk superalloy – Influence of aging heat treatment and local chemical fluctuations F. Pettinari-Sturmel, W. Vultos, M. Hantcherli, B. Warot-Fonrose, C. Marcelot, Joël Douin, J. Cormier, P. Villechaise, A. Devaux • Journal of Applied Physics, American Institute of Physics, 2018, 124 (23), pp.235309. DOI : 10.1016/j.msea.2019.02.088.May 2018

Nickel-based superalloys are widely used in aircraft and helicopter engines for their outstanding mechanical properties at operating temperatures around 750°C. To allow for ever higher temperature operations, new alloys are being developed. Their use imposes a fine understanding of the mechanisms of deformation. This is made possible by the investigation methods available at CEMES.



Creep tests at 700°C/500 MPa for the 3 heat treatments at 730°C, 760°C or 790°C (L. Thébaud, PhD Thesis ENSMA-PPrime, Poitiers). Precipitates/matrix concentration profiles and TEM observations of the deformation mechanisms in the samples aged at 760°C (a) and 790°C (b)

These superalloys mainly contain nickel but also a very precise proportion of other elements such as chromium, cobalt or titanium. When analyzed at the microscopic scale, they appear to consist of a matrix and hardening precipitates. Research to date has correlated the characteristics of these precipitates with microscopic strain mechanisms and mechanical properties. However, the different chemical species are distributed between the two phases and their distribution can evolve under solicitation. The influence of the distribution of chemical elements at a very small scale remains scarcely studied, as well as the evolution of this distribution when the alloy is subjected to thermal and/or mechanical stresses, while it can produce tremendous changes. ompositions of the various phases (matrix and precipitates), an evolution has been evidenced when the alloy is heat-treated at 790°C. This evolution of chemical composition has been related to the physical parameters that control the micromechanisms of deformation and thus allowed to explain the decrease of lifetime of the alloy when heat-treated at such temperature.

This work proves the need to carry out fine analyzes of local chemistry coupled with identification of the deformation micromechanisms to improve the understanding of the mechanical behavior of these efficient materials.

This work take part in the cross study INCA INfluence of local Chemistry on the mechanical behavior of metallic Alloys.

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Diamanoïds: A new-born in the nanocarbon family

A solution to overcome graphene limitations in electronics

Low temperature, pressureless sp2 to sp3 transformation of ultrathin, crustalline carbon films.

Piazza F., Gough K., Monthioux M., Puech P., Gerber I., Wiens R., Paredes G., Ozoria C. Carbon 145, 10-22 (2019)

Towards a better understanding of the structure of diamanoïds and diamanoïd/graphene hybrids. Piazza F., Monthioux M., Puech P., Gerber I.

• Carbon 156 (2020) 234-241

Diamanoïds are nanosized sp3 carbon films whose possible occurrence was predicted in 2009 as the result from the hydrogenation of graphene (sp2 carbon) films. They exhibit a tailorable gap in function of the number of layers, which may allow ruling out the intrinsic issue related to graphene, which is a zero-gap material and there-by is useless as such for electronic applications. The combined efforts of the Labo-ratorio Nanociencias from the PUCMM (Dominican Republic), CEMES and LPCNO (Toulouse), and the University of Manitoba (Canada) have resulted in the successful synthesis of diamanoïds.



(a) and (b): Model (brown = C; pink = H) of a portion of a 6-layer diamanoïd/graphene hybrid film (two other L2-L1 layers should be added below L4). (c) The structure of L1 + L2 is that of diamond oriented according to [111]. L3 and L4 are graphenes, but L2 exhibit pending pz orbitals (in yellow in (b)) which strongly interact with L3.

Because electronics is based on the transis-tor as its main component, it requires semi-conducting materials, in which the ener-gy difference between the valence and the conduction bands (named gap) is low, al-lowing electrons to be transferred at will from the former to the latter by applying an external electrical field. an external electrical field.

The diamond form of carbon (sp3 hybri-dised) is an insulating material because its gap is high (5 eV), which does not allow the material electrons to contribute to the overall conductivity. On the other hand, the graphenic form of carbon (sp2 hybri-dised) has no gap, making it a conducting material. Therefore, none of those two forms are suitable for electronic applica-tions, in spite of the high expectations put in graphene in the field. in graphene in the field.

In 2007 was predicted the existence of a stable form of hydrogenated graphene, so-called graphane, which consists in a single-atom layer of sp3 carbon atoms, each of a bilayer graphene could induce the sp3 to sp2 conversion of the carbon atoms, resulting in a stable bilayered material in which half of the bonded to carbon atoms from the other layer. This material was named diamane, and exhi-bits either the diamond (face-centred cubic) or lonsdaleite (hexagonal) structure, depending on whether the initial graphene stacking sequence is AB (as in graphite), or AA respectively. If the initial graphene is made of N layers (N > 2), it was also predicted that the sp2asp3 for the conversion to propagate within inner layers, resulting in a film-like material which structure is either diamond or lonsdaleite of nanosized thickness with both surfaces hydrogenated. Such materials had been convincingly successful so far.

The Laboratorio Nanociencias from the Pontificia Universidad Catolica Madre y Maestra (Do-minican Republic), CEMES and LPCNO (Toulouse), and the University of Manitoba (Canada) have combined their research efforts to demonstrate, for the first time, the successful syn-thesis of diamanoïds, as well as diamanoïd/graphene hybrids, using a low temperature, low pressure hydrogenation process (PUCMM patent). The hydrogenated character of the sur-faces as well as the complex inner structure of the materials obtained were demonstrated by comparing DFT-based modelling to experimental data obtained from Raman spectroscopy (visible and UV), infrared microscopy, and low energy (5 keV) electron diffraction. The next step will aim at demonstrating the successful synthesis of diamane starting from bilayer graphene, as soon as such a material with suitable quality is available.

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Wires or islands in the Stranski-Krastanov growth mode? It is a matter of surface energy Published in Appl. Phys. Lett.

Shape transition in InAs nanostructures formed by Stranski-Krastanow growth mode on InP (001) substrate A. Ponchet, L. Pedesseau, A. Le Corre, C. Cornet and N. Bertru.

• Appl. Phys. Lett. 114, 173102 (2019) https://doi.org/10.1063/1.5091058

The frequent formation of InAs wires during the Stranski-Krastanov growth of InAs on InP substrates was attributed to the surface diffusion anisotropy of indium atoms. We propose a model integrating the anisotropy of the InAs surface energy. Without resorting to any kinetic mechanism, our model predicts a wireto-island shape transition in agreement with the experimental observations.



Equilibrium shape (length L^{ES}, width W^{ES} and height h^{ES}) as a function of the volume of InAs nanostructures grown on InP(001) substrates, determined for the indicated InAs surface energy densities. AFM experimental images 300 nm x 300 nm. To account for wire formation and wire-to-island shape transition observed during the growth of InAs on (001)InP substrates, an experimental study was combined with an analysis based on an equilibrium shape model.

Due to the 3.2% misfit, the growth mode by molecular beam epitaxy (MBE) is Stranski-Krastanov (SK) (formation of InAs nanostructures). Formation of elongated wires rather than islands is frequently observed in the first steps of the SK growth mode. It was attributed to a kinetic mechanism, the anisotropy of surface diffusion of Indium atoms.

Our hypothesis is that the equilibrium shape itself varies with the volume of the InAs nanostructure, due to the anisotropy of surface energy of the lateral facets of the III-V nanostructures (A or B facets parallel to [-110] and [110] respectively). This surface energy anisotropy is considered to determine the nanostructure equilibrium shape from the balance between the elastic energy and the surface energy (calculated respectively by finite element method and by density functional theory DFT). At low volumes, the most energetically favorable shape is the wire-like shape, while at high volumes, the equilibrium

shape is the island-like shape. The calculated sizes for which the shape changes are in good agreement with experimental sizes from our experiments. The low lattice mismatch and the low surface energy of (114)A InAs facets around 41 meV/A2, as obtained from our DFT calculations, enhance this effect in the InAs/InP system.

Collaboration with FOTON, INSA Rennes.

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A 2nm helical molecular gear with an unidirectional rotation

Published in Nature Communications

A chiral molecular propeller designed for unidirectional rotations on a surface

rotations on a surrace
Y. Zhang, J.P. Calupitan, T. Rojas, R. Tumbleson, G. Erbland, C. Kammerer, T.M.
Ajayi, S. Wang, L.C. Curtiss, A.T. Ngo, S.E. Ulloa, G. Rapenne, S.W. Hla Nature Commun. 2019, 10, article n° 3742. doi:10.1038/s41467-019-11737-1

Claire Kammerer, Lecturer and Gwénaël Rapenne, Professor at Toulouse III University - Paul Sabatier, CEMES-CNRS laboratory, and at the Institute of Science and Technology of Nara (NAIST) in Japan and Saw-Wai Hla, professor at the University of Ohio, USA, have designed a molecular helix intended to be deposited on a solid surface and studied by scanning tunneling microscopy (STM). The chirality of this molecular machine makes it possible to control its direction of rotation once set in motion by a supply of electrical energy and this rotation could be transmitted to a neighboring molecule. This work was recently published in Nature Communications.



(a) Chemical structure of the molecular gear deposited on a gold surface; (b) STM images of the unidirectional rotation of each helix © G. Rapenne (UT3 Paul Sabatier, NAIST, CEMES-CNRS) and S.W. Hla (Ohio Universitu).

Synthetic molecular machines designed to work on surfaces are today able to convert energy into unidirectional movement but also under certain conditions, to transfer this movement to other molecules. In this study, ruthenium complexes designed to mimic gears deposited on a gold surface are in the form of a mixture of left and right helices in equal amounts. In figure (a), the heavily congested lower part (stator, in blue) is attached to the surface, it becomes helical and it transfers its helicity to the upper part (rotor, green) consisting of three blades that twist to satisfy the steric constraints of the stator part. The ruthenium atom plays a similar role to a ball-bearing. These propellers can be rotated in a highly unidirectional manner by providing energy via the tip of the STM. The left helical molecules rotate preferentially clockwise while the right helical molecules preferentially rotate in the opposite direction, as shown in the figure (b). Finally,

when a right helical molecule is placed at an appropriate distance from a left helical molecule, the rotational movement of a gear molecule could be transmitted to the neighboring molecule as shown in the video below. This observation could pave the way for the transfer of energy or information over long distances.

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 Mechanism of plasticity: when dislocations participate to the movement of grain boundaries

Published in Physical Review Materials

Heterogeneous disconnection nucleation mechanisms during grain boundary migration Combe, N.; Mompiou, F. & Legros, M > Phys. Rev. Materials, 2019, 3, 060601 (R)

When a metal deforms plastically, several families of mechanisms at the atomic scale operate. Among these, grain boundary migration is an efficient plastic mechanism in the absence of dislocation activity. This migration occurs through the nucleation and displacement of defects called disconnections. Atomic scale simulations have shown that a dislocation absorbed in a grain boundary could operate as a source of disconnections and thus facilitate the migration of a grain boundary.



The sessile disconnection δ operates as a source of glissile disconnections $\mu{<}110{>}$

When a stress is imposed on a metal, this latter deforms first reversibly, the elastic regime and then irreversibly, the plastic regime. Many applications (mechanical piece of a motor for example) require a high value of the critical stress above which one reaches the plastic regime. Thus, a fine understanding of the mechanisms of plasticity is necessary to improve the properties of materials.

The defects usually responsible of plasticity are called dislocations. The knowledge acquired over the past 70 years on the motion of dislocations has made it possible to design materials in which plasticity by movement of dislocations is practically inhibited and which are therefore extremely resistant: special steels, super alloys, nanocrystalline alloys. In these situations, it has been known for fifteen years that other mechanisms of plasticity can be activated. Among them, the migration of grain boundaries is currently the subject of intense research activity. For some years, the migration of the joints has been known to result from the

nucleation and the displacement of specific defects called disconnections, which combine a character of dislocation (elemental shear) and of step (lack of flatness). Using numerical simulation, the nucleation of these disconnections was studied on perfectly flat and defectless grain boundaries, which only rarely exist in real materials. Real joints contain vacancies, impurities, dislocations, steps, and of course disconnections. All these imperfections of the joint can potentially alter its migration mechanism by potentially creating some sources of inhomogeneous nucleation of disconnections.

By conducting molecular dynamics simulations at the atomic scale, a CEMES team proposed for the first time an inhomogeneous nucleation mechanism of disconnection from an imperfection of the joint created by the absorption of a dislocation. It has been shown that the presence of this imperfection significantly decreases the energy barrier necessary for the nucleation of the mobile disconnections

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Artificial proteins trained as nano-goldsmiths

Published in Nanoscale

ADirected evolution of artificial repeat proteins as habit modifiers for the morphosynthesis of (111)-terminated gold nanocrystals.

- J. Prasad, S. Viollet, G. K. L, A. Urvoas, A. Fournier, M. Valerio-Lepiniec, C. Garcia-Marcelot, B. Baris, P. Minard and E. Dujardinn.
- Nanoscale, 2019,11, 17485-17497 DOI: 10.1039/C9NR04497C

Artificial proteins selected for their chemical affinity for gold and their specific structural recognition of (111) atomic planes prove to be highly effective in controlling the growth of exclusively (111)-facetted nanocrystals. Strongly bound to the facets, they can be modified to induce colloidal self-assembly or on-surface enzymatic catalysis.



Artificial repeat proteins are selected by directed evolution for their high chemical affinity for gold and structural selectivity for (111) facets. The proteins chaperone the growth of (111)-terminated nanocrystals and form a functional shell.

Darwinian evolution explains the emergence of proteins that chaperone the growth and morphogenesis of biominerals (Ex.: enamel, bone, nacre) and dictate their surface properties.

Directed evolution is a combinatorial biochemical tool that mimic Darwinian evolution. Libraries of billions of peptides or antibodies, all distinct from each other and each embedded on a bacteriophage virus are built. When the bacteriophage population is exposed to a target (Ex. a pathologic antigen), directed evolution enables the identification of the few individuals, among several billions, that bind most strongly ("have the highest affinity") to the target. The peptide or antibody responsible for this extremely specific chemical recognition can then be synthesized. Directed evolution has revolutionized analytic and therapeutic biochemistry and has earned F. Arnold, G. Smith and G. Winter the Nobel Prize in Chemistry 2018. Yet, it is almost impossible for a flexible peptide or antibody to distinguish a specific crystalline order.

Directed evolution has been applied, for the first time, by two teams from CEMES (Toulouse) and IB2C (Orsay), to a library of fully folded artificial proteins exposed to the (111) atomic planes of crystalline gold surface. The library, built by the IB2C bioche-

mists, comprises about 2 billions repeat proteins that share a scaffold made of concatenated double alpha helix modules, which endows them with a much more rigid structure than antibodies, but that are distinct from each other by the set of amino acids present on the binding surface. The two teams have isolated, sequenced, and mass produced nine proteins with strong affinity for gold and more specifically for (111) crystal planes. When added to a gold nanoparticle growth solution, these proteins govern the nanocrystal shape (decahedra, icosahedra, plates) and size (50-500 nm) but more importantly the faceting resulting in more than 85% exclusively Au(111)-faceted nanocrystals. Importantly, the protein shell spontaneously assembled on the nanocrystal facets is exploited to drive protein-mediated colloidal self-assembly and on-surface enzyma-tic catalysis. These results, that have been published in Nanoscale (Royal Society of Chemistry), offer a generic and designable tool for producing nanocrystals with determined faceting, superior biocompatibility and versatile biofunctionalization towards plasmon-based devices and (bio)molecular sensors.

Collaborative work carried out within the ANR ARTEMIS project: https://anr.fr/Project-ANR-14-CE08-0004

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Sweet surfaces Carbohydrate self-assembly at metal surfaces

Carbohydrate self-assembly at surfaces : STM imaging of sucrose conformation and ordering on Cu(100) S. Abb, N. Tarrat, J. Cortés, B. Andriyevsky, L. Harnau, J. C. Schön,

- S. Rauschenbach, K. Kern
- Angewandte Chemie Int. Ed., 2019, 58, 1. Back Cover !

Polymorphism in carbohydrate self-assembly at surfaces : STM imaging and theoretical modeling of trehalose on Cu(100)

S. Abb, N. Tarrat, J. Cortés, B. Andriyevsky, L. Harnau, J. C. Schön, S. Rauschenbach and K. Kern

- ▶ RSC Advances, 2019, 9, 35813 35819

Saccharides are ubiquitous biomolecules, but little is known about their interaction with surfaces. By combining soft-landing electrospray ion beam deposition, scanning tunneling microscopy imaging and multi-stage modelling, the conformation and assembly patterns on Cu(100) of two disaccharides, sucrose and trehalose, were revealed.



1) STM image of the sucrose periodic network on Cu(100) at 40K. 2) Comparison of measured (left) with simulated STM images (center) and the molecular structures (right) of sucrose. STM image of trehalose assembly on Cu(100) at RT. 4) Measured (left) and simulated (right) STM images of motif B

partly overlaid with the molecular structure.

Saccharides, also known as carbohydrates, are ubiquitous biomolecules, but little is known about their interaction with surfaces. Soft-landing electrospray ion beam deposition in conjunction with high-resolution imaging by scanning tunneling microscopy (STM) now provides access to the molecular details of the surface assembly of this important class of biomolecules. As examples, sucrose - one of the most widely used ingredients in the food industry - and trehalose that exhibits strong effects on the anhydrobiosis of biosystems, were chosen for the study of their self-assembly on a Cu(100) surface. Sucrose molecules were found to be mobile at room temperature (RT) but after cooling to 40 K nearly all the molecules are assembled in 2D islands in form of periodic networks. In contrast, trehalose molecules already self-assemble at RT, and a variety of combinations of at least two basic compatible structural motifs is observed (a linear chain and a 8-molecule hollow square block). To shed light on the molecular

conformations and their assemblies, a multi-stage modelling procedure was employed. It was composed of global explorations of the potential energy landscapes using a new algorithm called IGLOO (a stochastic method that performs global optimization by iterating local searches) followed by DFT refinements, yielding energetically nearly equivalent conformations representing different possibilities for the disaccharides to adsorb on the surface. Applying the constraints of the STM observations, we rationalized which conformation is the observed one for each molecule, and constructed models for the intermolecular interactions. The specific knowledge gained about their adsorption geometry can help in understanding the influence of these saccharides on e.g. hydration/anhydrobiosis properties. At this resolution, the combination of STM with state-of-the-art multi-stage simulation methods is a very promising approach to characterize the structure of complex carbohydrates adsorbed on surfaces, such as those involved in the formation of bacterial biofilms. This highlight reports a joint research work of CEMES, LAAS and MPI Stuttgart.

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A new, full bottom-up approach for the analysis of X-ray diffraction patterns of graphenic carbons

Solving a 80-year-old problem

New insight on carbonisation and graphitisation mechanisms as obtained

from a bottom-up analytical approach of X-ray diffraction patterns. Puech P., Dabrowska A, Ratel-Ramond N., Vignoles G., Monthioux M.

Carbon 147 (2019) 602-611.

Graphenic carbons are of an utmost technological importance. Predicting their properties requires measuring the average crystallite dimensions, but the bidimensional nature of the turbostratic part of the often-complex crystal structure makes the analysis of diffraction patterns not straightforward. By using a predictive approach of the crustal structure, CEMES has come up with a new methodology which finally allows mowing away from a 80-year-long unsatisfactory empiricism.



The three different Basic Structural Components (BSC) of the average crystallite which varying the proportions allows any graphenic material to be described, whatever its degree of structural progress towards the ultimate graphite structure: the 'Turbostratic' BSC, for which each graphene contributes indivi-dually since the stacking sequence is in random rotation; the "AB pair" BSC, for which graphenes display by pairs within which the stacking sequence if that of graphite (AB), while pairs are turbostratically stacked; the "Bernal" BSC, for which all the graphene involved are stacked according to the ABAB... sequence of the hexagonal structure of graphite.

Graphenic materials are of an utmost technological importance for a broad variety of domains. They are obtained from the carbonisation of organic natural or synthetic precursors which elemental composition determines both the anisotropy degree of the material and its ability to ultimately reach the graphite struc-ture. From the very first steps of carbonisation, polyaromatic molecules develop and pile up as the embryos of graphene layers. Crystallites are then formed all over with similar dimen-sions (L_a , L_c) which are characteristic of the material. Meanwhile, the graphene stacking sequence may evolve from rotationally random (turbostratic structure) to partially or fully ordered (graphitic, hexagonal structure).

Many of the properties of a graphenic carbons thus depend on the average crystallite dimen-sions, more importantly La. Measuring the latter is therefore critical, usually by means of X-ray diffraction (XRD). Unfortunately, the bidimensional nature of the turbostratic part of the crystallite structure makes the analysis of XRD patterns an issue which was addressed over the last 80 years by developing a variety of fitting and correcting methods aiming at obtaining the La values, which all failed in being reliable and univocal.

For addressing the issue, CEMES has considered it the reverse way: instead of empirically fitting experimental XRD patterns by pre-existing functions for estimating the La (topdown approach), parametrised functions are created from atomistic modelling of the average crystallite, and then the computer is left free to calculate the related XRD patterns for a whole range of La (bottom -up approach). The calculated pattern which fits the experimental pattern at best provides the right La value. The key of success was to model the average crystallite as composed from a mixture of three Basic Structural Components (BSC) which proportions may vary: "Turbostratic", "AB pair", and "Bernal" (cf. Fig.). Thus, for a graphitisable carbon, the average crystallite evolves from 100% "Turbostratic" at early carbonisation stage (< 1500°C) to 100% "Bernal" at the end of graphitisation (~3000°C), while passing by combinations in which the three BSCs may coexist. The methodology also introduces new structural parameters such as the BSC pro-portions, and Lc' which characterises the height of the average "Bernal" BSC within the average crystallite on the path to graphitisation.

The methodology is valid for any type of graphenic material whatever the precursor and the degree of structural maturation.

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<u>CEMES events</u>

#80ansCNRS

On October 19, 2019, the CNRS celebrated its 80th anniversary. For 80 years, our knowledge has been building new worlds!

During 365 days, the CNRS celebrated, through events in France and abroad, the fundamental values of the institution: freedom of research, advancement of knowledge, teamwork, scientific excellence, innovation and technological transfer, social progress and dissemination of scientific culture.



This anniversary year was an opportunity to address all audiences through many events and meetings. CEMES celebrated this anniversary through two events: The inauguration of a joint laboratory with the Japanese company Hitachi and open days for schoolchildren and the general public.

September 24, 2019 Inauguration of the joint-laboratory Hitachi-CNRS on ultra-fast microscopy HC IUMi



Inauguration of the joint-laboratory Hitachi-CNRS on ultra-fast microscopy HC-IUMi in the presence of CNRS CEO Antoine Petit – September 24, 2019.

► One new microscope was inaugurated at CEMES as part of the first international joint laboratory between the CNRS and a foreign company: Hitachi.

➤ The unique partnership between CNRS and Hitachi High Technologies Corporation results in the creation of a joint laboratory and the installation at CEMES of the high-performance TEM used to developed the next generation of ultrafast TEM. On September 24, 2019, CEMES inaugurated the advanced HHT microscope on which will be transferred the coherent electron source developed in the laboratory.

▶ This inauguration celebrates the 80 years of the CNRS by highlighting the value of research.

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CEMES events

CEMES open days

Friday 11th and Saturday 12th October 2019

▶ 100 students and more than 600 people visited the CEMES during our open days: a great success for this special edition to celebrate the 80 years of the CNRS!

▶ Visitors could choose from 10 workshops including two for children, as well as a plenary lecture. Most stayed no less than two hours in the laboratory and could see electron microscopes or spectrometers, exchange with researchers and visit the famous historical electric generator!





<u>CEMES members awards</u>



Florent Houdellier Ernst Ruska Award 2019

The Ernst Ruska 2019 Prize from the German Microscopy Society is awarded for his contribution to the development of a new ultra-bright pulsed TEM microscope based on cold FEG technology. Thanks to the unrivaled brightness of this source, this microscope has been used to acquire the first holograms with femtosecond electrons pulses which motivated the attribution of this prize.

His work has been done in close collaboration with Dr. Arnaud Arbouet (CEMES, Toulouse) and Dr. Giuseppe Mario Caruso (CEMES, Toulouse), Dr. Sébastien Weber (CEMES, Toulouse) and Dr. Mathieu Kociak (LPS, Orsay).

European Microscopy Society Outstanding Paper

The European Microscopy Society Outstanding Paper Award has been presented to Florent Houdellier and Arnaud Arbouet for their publication in Ultramicroscopy.

F. Houdellier, G. M. Caruso, S. Weber, M. Kociak, A. Arbouet, "Development of a high brightness ultrafast Transmission Electron Microscope based on a laser-driven cold field emission source" Ultramicroscopy 186 (2018) 128-138.



Andrej Jancarik ICT Prize

The prize "Young investigator award 2019 ICT" was given to Andrej Jancarik, postdoctoral CEMES for his work on the new ways of synthesis of alkenes.

This award from the "Institut de Chimie de Toulouse" was set up in 2011 to distinguish the quality of research conducted by a young researcher. The Young Investigator Award from the "Institut de Chimie de Toulouse" consists of a grant (up to \in 1,500) to cover registration, travel and accommodation costs at an international congress. In addition, the laureate will present a seminar to the community at the beginning of the summer on the "ICT day" (2 July 2019).

<u>Few CEMES projects</u>

Collaborative Research between CEMES and Soitec



As a long-standing partner of CEA / Léti and Soitec in the development of the Smart Cut technology, CEMES strengthens its collaborative links with Soitec and is now committed to a three-year partnership around two Cifre doctoral theses. The first aims to further reduce the defect density of silicon wafers (FDSOI), the second to preserve or restore the piezoelectric properties of certain materials after implantation.

For more than 30 years, researchers at CEMES have been working on ion implantation, defect formation, the diffusion and precipitation of implanted impurities, and CEMES thus significantly contributed to the state of the art of the field at the international level.

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Ô-GST: Materials Science for Phase Change Memories

CEMES joins STMicroelectronics within the EC IPCEI Project on Microelectronics.



The standard built-in flash memory devices used in the automotive and Internet Of Things (IOT) industries are facing, at the most advanced technology nodes (28 nm and below), difficult physical challenges limiting switching speed, energy consumption and costs. Phase change memories (PCMs) are emerging as a promising alternative technology to overcome these limitations. These PCM memories use thin layers of chalcogenide

alternative technology to overcome these limitations. These PCM memories use thin layers of chalcogenide materials, a GeSbTe alloy (GST), which is locally and reversibly switched between its crystalline and amorphous states using electrical pulses (Joule heating). The information is contained in the marked difference in electrical conductivity between the crystalline and amorphous phases of this alloy.

The ambition of the project is to provide European microelectronics companies with a foundation of knowledge in materials science to optimize the composition and processing of GeSbTe-based alloys used in the manufacture of phase change memories.

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esteem3 H2O2O Integrated Infrastructure (INFRA-IA) Project

Jan. 2019 to Dec. 2022

ESTEEM3 "Enabling Science and Technology through European Electron Microscopy" is the continuation of the ESTEEM (2005-2011 / FP6) and ESTEEM2 (2012-2016 / FP7) projects with and enlarged European consortium of 15 academic partners and 5 companies. ES-TEEM3 aims to provide access for the academic and industrial research community in materials science to the most powerful TEM techniques available at the nanoscale. It also will carry out Joint Research Activities (JRA) on selected areas in TEM techniques and issues (imaging, diffraction, métrology, spectroscopy, in-situ TEM, data treatment and microscope automation) and specific applications i.e. material for ICT, material for Energy, material for Health, and material for Transport.

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Clean room facilities at CEMES



Clean room facilities at CEMES



Nanofabrication and Atom Tech platform

The Nanofabrication and Atom Tech (NAT) platform at CEMES aims at providing expertise, tools and instruments dedicated to micro- and nanofabrication for basic and applied research, education and training. The platform is a 400m2 cleanroom type laboratory; segmented in several dedicated rooms classified as ISO Class 4 to 7, the ISO 4 room is dedicated to current lithography processes and advanced atom tech elaboration.

The NAT platform is open to the global scientific community both for academic researchers within or outside CEMES and for industries.

Experimental techniques available

► Nanofabrication: the NAT platform provides the main tools to design and elaborate nanodevices, such as photolithography (laser, mask aligner), electron beam lithography, wet etching, ion beam and reactive ion etching (IBE - RIE), focussed ion beam (FIB), physical vapour deposition (electron beam evaporation, sputtering), focussed ion beam induced deposition (FEBID), and characterization techniques such as optical microscope, mechanical profilometry, scanning electron microscopy, atomic force microscopy, electric characterizations...

 Atom Tech: In addition to micro-fabrication by classical lithography techniques, the NAT platform provides access to UHV-based nano-tools, such as nano-stencil through suspended diaphragms or pierced AFM cantilevers, and nano-printing.

► The preparation of the surfaces necessary for the development of nanodevices is made by UHV metal and insulator deposition machines. UHV chamber interconnects allows to obtain the picometric precision necessary for the study of atomic circuits, and mechanical molecule-machines.

NAT platform and People Skills

Thanks to its unique dedicated equipment and expertise, the NAT platform offers:

► The development of custom nanofabrication process of nanodevices based on thin films, nanostructured materials, nano-objects for applications in optics, magnetism, radio frequency, transport properties, in-situ transmission electronic microscopy studies under electric or magnetic excitation, ...

► The development of original processes in a full high vacuum compatible nanofabrication line for nanoscience with the fabrication of ultra small epitaxial nanostructures, molecular electronics, atomic circuits, mechanical molecule-machine, ...

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NanoX graduate school

NANOSCALE SCIENCE AND ENGINEERING

CEMES is an active partner of the NanoX graduate school project, which started this year.

NanoX aims offering an innovative and high-level education program to motivated and talented students from France and all around the world, in the Nanoscale Science and Engineering domains, mainly at the master/graduate level.

The mission of this Toulouse graduate school in Nanoscale Science and Engineering is to bring together the key forces in research and education in Toulouse from a leading university (UPS), two well recognized engineering schools (INSA and INP-ENSIACET) and the main French national research organism (CNRS) the CEMES belongs to. This will give new opportunities to the master and PhD students involved in NanoX.

In short, NanoX will:

- Promote Toulouse as an international high level training centre in Science and Engineering at the Nanoscale by:
 - Promoting learn-by-doing and training-by-research teaching
 - Introducing advanced courses and favouring interdisciplinarity
 - Increasing the synergy between research and training for research-oriented studies in Nanoscale Science and Engineering
- > Stimulate the incoming and outgoing international mobility of master or PhD students
- Strengthen relationships with the socio-economic world
- Contribute to strengthen reciprocal relationships with other international universities both at the MSc and doctoral levels
- Prepare master students for doctoral studies at the crossroads of Chemistry, Physic Material Sciences, both experimentally and theoretically
- Stimulate the creation of brand new courses, including by a scientific and technical monitoring
- Render students skilled in the design, the modelling, the characterization, the fabrication, and the addressing of innovative nano-objects with tailored properties

One objective of NanoX is to create in 2021 an international multidisciplinary Nanoscience and Nanotechnology MSc degree, aiming at attracting talented international students in our MSc degrees and in our labs.

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